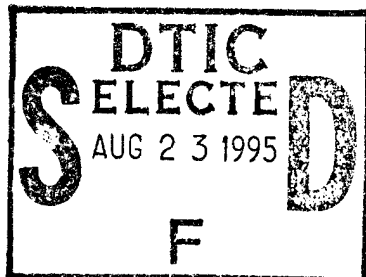


**Evaluation of early diagenesis in modern, shallow-water carbonate
sediments by mineralogy, fabric and porewater geochemistry**

by

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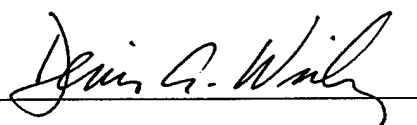


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1. Introduction

Early diagenesis is an important process affecting the coastal benthic boundary layer. Variation in sediment mineralogy and fabric due to the geochemical processes during early diagenesis can alter sediment physical properties and therefore have an impact on mine countermeasure systems that are of great interest to Navy.

The Naval Research Laboratory (NRL) is presently conducting a comprehensive study of the coastal benthic boundary layer. Our research is undertaken in conjunction with that NRL study known as the Coastal Benthic Boundary Layer special Research Program (CBBLSRP). Our particular study investigates the effect of geochemical processes on sediment fabric and mineralogy in a carbonate platform environment of the Key West area. Early studies indicated that shallow carbonate sediments that have been in contact only with seawater throughout their history show no evidence for diagenetic reactions (e.g., Berner 1966). However, more recent studies have revealed the possibility of volumetrically significant dissolution and recrystallization of carbonate minerals during the early diagenesis of shallow carbonate sediments (e.g., Walter and Burton, 1990).

The purpose of this study is to quantify the extent of early diagenesis in the carbonate platform sediments of the Key West area and to identify the mechanisms responsible for diagenetic reactions, such as dissolution and recrystallization of the carbonate minerals. In order to achieve these goals, mineralogy, fabric and porewater geochemistry of the sediment cores from the areas are being extensively investigated. This quarterly progress report presents the results from the investigation and indicates the plan for the rest of the grant period.

2. Methodology

The author participated in the CBBLSRP Key West Campaign that was conducted in the area of carbonate sediments of Dry Tortugas and Marquesas Keys, west of Key West, Florida, on board the German research vessel WFS *Planet* in February 1995. Sediment samples were obtained from the upper 2 m using box cores and gravity cores. Porewater samples were obtained from the upper 30 cm of sediment using Jahnke-type porewater squeezers (Jahnke, 1992). Porewater samples were collected and processed on board WFS *Planet*. Sediment samples from box cores were collected by Dennis Lavoie of Naval Research Laboratory and the author. Sediment samples from gravity cores were collected by Dawn Lavoie of Naval Research Laboratory on board R/V *Pelican* during the CBBLSRP Key West Campaign. Cores KW-PL-BC-141, 165, 194, KW-PL-DC-179 are from the Dry Tortugas area and KW-PL-BC-208 is from the Marquesas Keys area. Water depths in the study area are approximately 30 m.

Sediments from the study area are mixtures of macroscopic shells and shell pieces, and sand-, silt- and clay-sized carbonate particles (Kevin Stephens, pers. comm.). Extensive bioturbation and bioirrigation of burrow networks are present. Aragonite, Mg-

calcite and low-Mg calcite are the predominant mineral phases with minor quartz in some cores. Organic carbon content of the sediments is less than 1 weight % (Kathleen Fischer, pers. comm).

Porewater samples were drawn from a core squeezer that prevented samples from exposure to air. Porewater samples were analyzed for intermediate sulfur species and total reduced sulfur species using iodometric titration within 10 minutes of the sampling, and major and minor cation concentrations were determined using inductively coupled plasma spectroscopy (ICP) by Chuck Holmes at US Geological Survey Denver Office. The porewater samples were also analyzed for pH within 10 minutes of sampling.

Sediments from both box cores and gravity cores were sampled for the study of mineralogy and fabric. Mineralogy is studied using X-ray powder diffraction and subsequent Rietveld crystal structure refinement. Fabric is studied using petrographic microscope and scanning electron microscope (SEM).

3. Results and Progress

Porewater chemistry

Table 1 shows pH and the concentrations of reduced sulfur species for the porewater samples. Table 2 shows the results of ICP analysis. The reduced sulfur species concentrations indicate that sulfate reduction and reoxidation occur at and below 3 cm from the water-sediment interface. Major cation concentrations show little variability through the sampling depths. Variability in Ca^{2+} concentration was more pronounced and used as evidence for carbonate dissolution in studies of Florida Bay carbonate sediments (e.g., Walter and Burton, 1990).

X-ray powder diffraction mineralogy

The X-ray powder diffraction indicated that the sediment samples are composed of calcite of various Mg contents and aragonite, with occasional minor quartz. Figure 1 is a part of the X-ray diffractograms of samples from the box core KW-PL-BC-194 that shows peaks of aragonite and high- and low-Mg calcite. Quantitative phase analysis is underway on the diffractograms by Rietveld crystal structure refinement. Rietveld refinement will also yield accurate cell constants for calcite that can be used to determine mole % MgCO_3 in calcite (Reid et al., 1992; Goldsmith and Graf, 1958).

Optical microscopy

The optical microscope observation of a gravity core from Dry Tortugas revealed a bimodal distribution of carbonate grains within the cores from both Marquesas and Dry Tortugas. Large grains (>1 mm) are mostly shells and shell fragments whereas matrix (50

~ 300 μm) are mostly algae fragments. Grains to matrix ratio is approximately 1 to 4 throughout the observed depths (0 to 130 cm below seafloor).

SEM

SEM photographs of gravity core samples indicate the presence of micritic cement in the samples from Dry Tortugas at the depth of 130 cm (Figure 2). A cloudy mass that looks like an aggregate of fine grain material is present among grains in the samples from 130 cm below seafloor whereas such mass is absent in the samples from near water-sediment interface. Further SEM analysis is planned in order to estimate the amount of micritic cement.

4. Discussion and Plans

Estimation of the extent of diagenetic reactions

The porewater data indicate that the concentrations of major solutes such as Ca^{2+} and Mg^{2+} are nearly constant within the top 30 cm of the sediments. The constant depth profile of porewater chemistry in carbonate sediments was originally interpreted as one of the evidences for the lack of diagenetic reactions in shelf carbonate sediments of Bahamas (Berner, 1966). However, the SEM image of the sample from 130 cm below seafloor (Figure 2) indicates the presence of micritic cement in the present study, suggesting that the major element chemistry in porewater may not be a sensitive indicator of the extent of diagenesis. This lack of sensitivity is probably due to the extensive bioturbation and bioirrigation observed in the study area.

Therefore in the present study, the extent of diagenesis will be estimated using the Mg content of calcite, that should differ between the primary biogenic calcite and recrystallized diagenetic calcite. Recrystallized diagenetic calcite should be in kinetic equilibrium with the porewater (Walter and Morse, 1984), whereas the biogenic calcite is not. Accurate Mg content of calcite can be calculated using the cell constants of calcite, which is derived using Rietveld crystal structure refinement method (e.g., Bish and Post, 1993).

5. Summary

SEM observations suggest fairly extensive recrystallization of carbonate minerals within the upper 130 cm of the sediments in the study area. Major cation concentrations such as $[\text{Ca}^{2+}]$ are insensitive to the early diagenesis and cannot be used as the measure of the extent of diagenesis in the study area. Rietveld crystal structure refinement will be used in the present study to quantify the extent of phase transformation in terms of mineralogy.

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Table 1. Sulfur speciation and pH of porewater samples.

Core	Depth (cm)	Total Aqueous Reduced Sulfur* ¹ (mM)	Intermediate aqueous Sulfur * ² (mM)	pH
KW-PL-BC-141	1	<0.1		
	2			7.63
	6			7.69
	7	0.1		
	10			7.66
	13	<0.2		
	14			7.74
	18	0.4		7.79
	22	0.8		7.76
	26	0.2		
	30	0.9		
KW-PL-BC-165	3	<0.02		7.63
	7	<0.02		7.88
	11	<0.02		7.77
	15	<0.02		
	19	0.04		7.84
	28	0.02		
KW-PL-DC-179	1			7.53
	3		0.01	
	5			7.67
	7		0.04	
	9			7.68
	11		0.05	
	13			7.75
	15	0.11	0.06	
	17			7.71
	19		0.07	
	22			7.80
	24		0.04	
KW-PL-BC-194	3	<0.02	0.01	7.76
	7	0.04	0.03	7.57
	11	0.04	0.03	7.74
	15		0.03	7.80
	18			7.93
	19		0.03	
	22			7.82
	23	0.10		
	26			7.77
	28		<0.03	
KW-PL-BC-208	1			7.74
	5			7.72
	13			8.05
	17			7.96
	22			7.99

$$*^1 = 2\Sigma[\text{S}^{2-}] + 2[\text{SO}_3^{2-}] + [\text{S}_2\text{O}_3^{2-}]$$

$$*^2 = 2[\text{SO}_3^{2-}] + [\text{S}_2\text{O}_3^{2-}]$$

Table 2. Results of ICP analysis.*

Core	Depth (cm)	B (ppb)	Ca (ppm)	K (ppm)	Li (ppb)	Mg (ppm)	Na (ppm)	Si (ppm)	Sr (ppb)
KW-PL-BC-141	2	3700	460	410	<200	1300	9800	5.0	8400
	6	4600	520	470	200	1400	11000	4.9	9500
	10	3900	470	420	210	1300	10000	4.1	8400
	14	4000	470	420	<200	1300	10000	4.9	8500
	18	3900	470	420	<200	1300	10000	4.7	8200
	22	4100	490	450	210	1400	11000	5.3	8500
KW-PL-BC-165	3	4000	500	450	230	1400	11000	5.7	8900
	7	4500	540	490	270	1500	12000	5.1	9300
	11	4200	510	470	<200	1400	11000	4.3	8900
	15	3500	470	430	240	1300	10000	4.5	7800
	19	4100	510	460	220	1500	11000	4.2	8700
	24	4000	500	450	<200	1400	11000	3.3	8300
KW-PL-DC-179	1	3600	520	440	220	1400	11000	4.3	8800
	5	4000	510	450	220	1400	11000	5.8	8700
	9	3600	470	410	200	1300	10000	5.1	8000
	13	3500	470	410	<200	1300	10000	3.5	7900
	17	3700	470	430	200	1400	10000	3.8	7900
	22	3900	500	450	<200	1400	11000	3.7	8500
KW-PL-BC-194	3	3900	520	450	200	1400	11000	4.8	8900
	7	3800	510	440	260	1400	11000	8.3	8600
	11	3900	500	440	200	1400	11000	4.8	8600
	15	3500	460	410	200	1300	9800	3.6	7800
	18	4400	540	480	<200	1500	11000	3.2	9300
	22	3700	480	420	<200	1400	10000	3.0	8200
	26	3300	450	400	210	1300	9600	2.9	7600
KW-PL-BC-208	1	3700	480	430	<200	1400	10000	4.6	8400
	5	3200	440	390	<200	1200	9300	9.0	7400
	13	3200	440	410	<200	1300	9600	5.1	7400
	17	3400	470	410	200	1300	10000	4.9	7700
	22	3900	520	470	220	1500	11000	4.6	8600

*The following elements were analyzed for, but below detection limits (detection limit); Al (10 ppm), Ba (400 ppb), Be (400 ppb), Cd (400 ppb), Co (800 ppb), Cr (800 ppb), Cu (2000 ppb), Fe (10 ppm), Mn (800 ppb), Mo (2000 ppb), Ni (2000 ppb), P (10000 ppb), Pb (2000 ppb), Ti (4000 ppb), V (800 ppb), Zn (800 ppb).

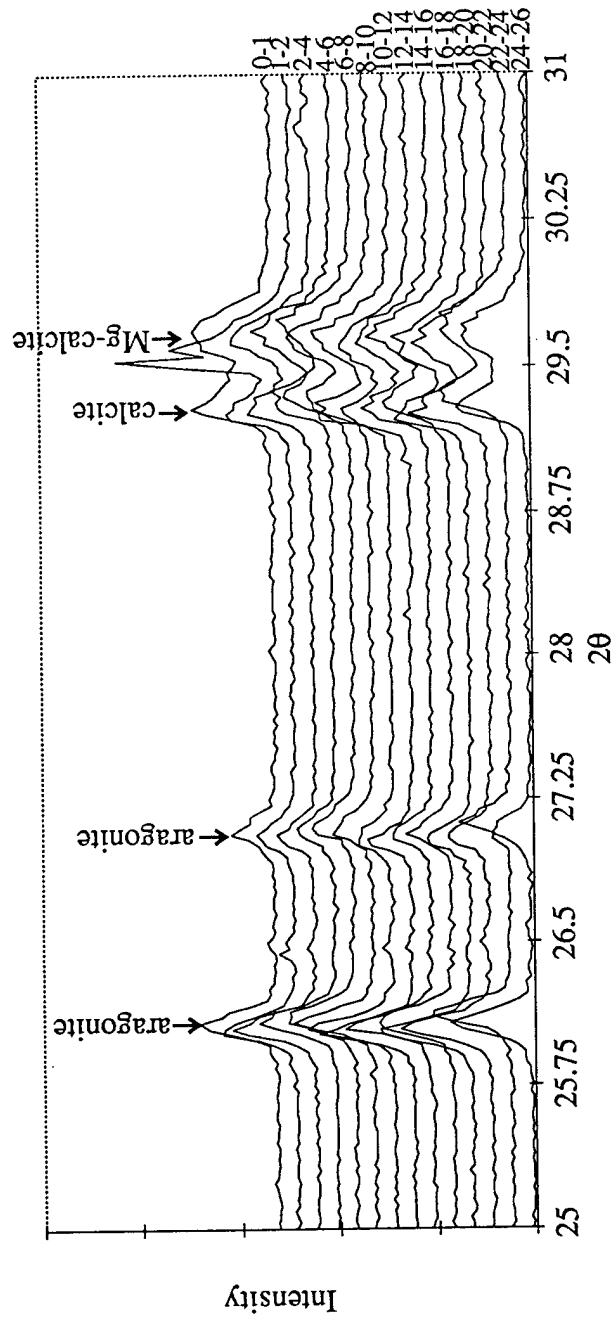


Figure 1. Portions of the X-ray diffractograms of core KW-PL-BC-194 showing aragonite and high- and low-Mg calcite peaks. Numbers on the right indicate the sample depths in cm.



Figure 2a. Polished section of a surface sediment sample from Dry Tortugas. Cement is absent. SEM.

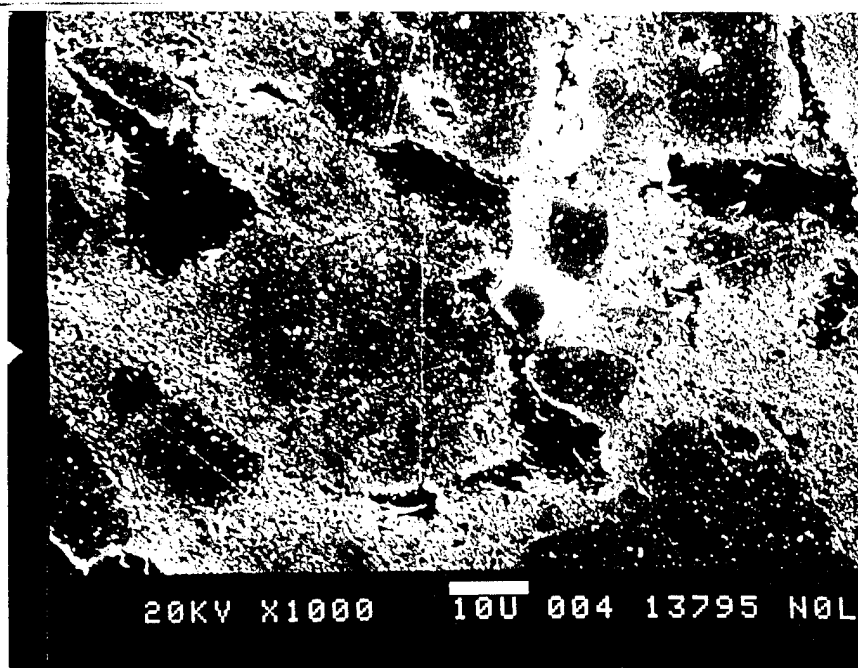


Figure 2b. Polished section of a sediment sample at 130 cm below seafloor. Cloudy aggregates of fine grain material are filling the pore space among grains and intimately attached to the grain surfaces. SEM.

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